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ELASTIC PROPERTIES OF SILICA XEROGELS

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## Elastic Properties of Silica Xerogels

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### Abstract

Longitudinal and transverse acoustic wave velocities have been measured for silica xerogels as a function of relative humidity in order to calculate elastic constants. The silica xerogels studied are microporous with open porosity of 53 vol %. The longitudinal wave velocity exhibits a minimum at about 35% RH (relative humidity). The transverse wave velocity decreases to a constant value for 35% and greater relative humidity. Consequently, Young's modulus is a minimum at 35% RH while the shear modulus decreases to a constant value at 35% RH. The bulk modulus and Poissons' ratio exhibit minimum values at about 15% RH. Young's modulus decreases from 4.91 GPa to 3.42 GPa at 35% RH and then increases to 3.60 GPa at 55% RH. Poisson's ratio decreases from 0.184 to 0.164 at 15% RH and then increases to 0.272 at 55% RH. Below 35% RH, silica xerogels adsorb a monolayer of hydroxyls while above 35% RH silica xerogels show pore filling.

## Introduction

The mechanical behavior of microporous materials prepared by the sol-gel process is largely uninvestigated, aside from some flexure strengths which have been reported for gels prepared by polymerizing tetraethylorthosilicate (TEOS). For wet gels, where the solvent remained in the pores, the modulus of rupture increased from less than 0.004 MPa to over 0.007 MPa in 7 days of aging (1). The same polymerized gels following drying and outgassing had strengths of over 20 MPa (2). From the time of gelling to becoming rigid and dry, the strength increased over 1000 times. The corresponding increase in Young's modulus was from 0.008 MPa for the wet gel (1) to about 5 GPa for the dried, outgassed xerogel (2,3).

The mechanical behavior of gels, especially after they are dried, is dependent on the environment in which they are used. Therefore, it is important to characterize mechanical behavior of xerogels as a function of exposure and relative humidity. It is often observed that dried gels, especially those that have not been outgassed or heat treated, will spontaneously crack. This behavior indicating a gradual or abrupt decrease in strength needs to be understood so it can be prevented.

The mechanical properties of porous materials, in general, are hard to predict, let alone those in xerogels which are microporous materials. As yet, the effect of porosity on their mechanical behavior has not been modeled though some properties have been reported (4,5). In fact, only recently have theoretical models been applied to the mechanical behavior of other porous gels, such as aerogels (6-10) and colloidal gels (11). Flexure strength and elastic moduli of aerogels and colloidal gels decrease with increasing porosity. Similarly, the strength and shear modulus of wet gels have been found to decrease with increasing porosity (1,12). Models developed for conventional ceramics such as



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Hashin and Shtrikman (13) have demonstrated that in addition to porosity, there are other shape parameters which also influence mechanical properties. Some parameters that have been mentioned are connectivity of ultrastructure, particle coordination number, particle radius and neck radius. No specific model has been developed for xerogels, though the models being developed for aerogels may apply (7).

As mentioned, there are a few studies that report mechanical behavior in gels as a function of porosity, moisture adsorption and impregnation of porosity. In one case, elastic properties of xerogels have been measured as a function of relative humidity (3). Otherwise elastic properties of xerogels (4,5), aerogels (6-8) and colloidal gels (11) have been measured as a function of porosity. Aerogels have a Young's modulus less than 1 GPa (6) and colloidal gels have Young's moduli between 0.3 GPa and 7.1 GPa (11). The shear modulus of wet gels has been measured as a function of aging and drying (1,12). In addition, Young's modulus of silica xerogels impregnated with polymethyl methacrylate (PMMA) has been measured (14). These xerogels were prepared from hydrofluoric acid catalyzed TEOS solutions. Xerogels before densification were about 70 vol % porosity with a pore diameter of 16.0 nm. Porosity was varied from 70 to 30 vol % by heat treatment, following which the xerogels were impregnated with PMMA.

#### Experimental Techniques

The preparation of samples has been described previously (15). Microporous rod shaped silica xerogels were prepared from nitric acid catalyzed solutions of TEOS. The molar ratio of water to TEOS was 16. All samples were ground lengthwise on opposite sides with 600 grit abrasive paper to produce slab samples of about 4 mm thickness. After grinding, porous silica xerogels were outgassed

again and stored in sealed tubes. Immediately after outgassing, xerogels had a bulk density of  $1.06 \text{ g/cm}^3$ , open porosity of 53 vol %, and a specific surface area of  $900 \text{ m}^2/\text{g}$ . Porosity was almost completely microporous (less than 2.0 nm in diameter) and cylindrical in shape.

Longitudinal and transverse wave velocities were measured with ultrasonics\*. Acoustic wave velocities were determined from measures of sample thickness and pulse transmission time. Transducers used in the pitch/catch mode were 5 Mhz (WC50-5) for longitudinal and 2 Mhz (SDB25-2) for transverse wave velocities. All measures were made without any coupling other than the dry coupling surface of the transducers themselves. For each test, five samples were measured and three measures of pulse transmission were made per sample. Porous xerogels were measured within 3 minutes of exposure with about 0.5% weight gain and also under conditions of exposure. Relative humidity varied naturally. Ambient relative humidity was measured with a digital hygrometer (Vaisala HMI 32) as calibrated with a sling psychrometer and recorded at the nearest even division of 5% RH. Porous xerogels were occasionally removed from the sealed tubes and exposed to 15, 35, 55, and 25% RH in that sequence at ambient temperature of  $23^\circ\text{C}$ . In each case, no further weight gain was recorded after 2 days. Between exposures the samples were stored in sealed tubes. The initial measurements were made after about 2 weeks and the final measurements were made after 3 months. Young's modulus,  $E$ , and shear modulus,  $G$ , were calculated from the longitudinal wave velocity,  $v_L$ , transverse wave velocity,  $v_T$ , and bulk density,  $p$ , according to (16)

$$E = (3pv_L^2 - 4pv_T^2)/((v_L/v_T)^2 - 1) \quad (1)$$

and

$$G = pv_T^2 \quad (2)$$

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\*Ultrason Laboratories, State College, PA

Poisson's ratios,  $\nu$ , and bulk modulus,  $K$ , were then determined from the relations:

$$\nu = (E/2G) - 1 \quad (3)$$

and

$$K = E/(3(1 - 2\nu)). \quad (4)$$

The sample bulk density was calculated two ways. First, the matrix bulk density was calculated by correcting the measured value of bulk density of a freshly outgassed sample ( $P_{\text{meas}}$ ) with a measure of linear contraction ( $l_0/(l_0 + \Delta l)$ ) assuming isotropic shrinkage.

$$P_{\text{matrix}} = P_{\text{meas}} (l_0/(l_0 + \Delta l))^3 \quad (5)$$

The total bulk density was calculated by including the weight gain of water ( $\Delta m$ ).

$$P_{\text{total}} = P_{\text{matrix}} + \Delta m P_{\text{meas}} \quad (6)$$

The way in which the density was calculated influenced the values of elastic constants  $E$ ,  $G$  and  $K$ .

### Results

When exposed to air, the xerogels gained weight by adsorbing moisture. The weight gain was reversible and roughly linear up to 55% RH with a value of 37% at about 55% RH. Weight gain increased proportional to the square root of time until equilibration at each relative humidity. Two of the 5 specimens exposed to 55% RH cracked and two more cracked when returned to 25% RH. The number of

measures of wave velocity per sample was increased to compensate for this decrease in population at these relative humidities. After exposure to 25% RH, the remaining sample was exposed to about 65% RH and a weight gain of 42% was observed. For comparison, the weight gain of a xerogel saturated with water from immersion was 49%.

Porous xerogels contracted upon aging in ambient atmosphere. Linear contraction increased from 0.3 % at 35% RH and two weeks aging to 2.0% at 55% RH and three months aging. Linear contraction increased to a net of 2.5% on return to 25% RH and then decreased to a net of 1.4% at 65% RH. For comparison, saturated samples exhibited linear expansion of 0.6% when soaked in ethanol and 1.2% when soaked in water.

In Table 1, the measured wave velocities are listed. In Figure 1, the change in wave velocities is shown as relative humidity was varied from 0 to 55% RH. The transverse wave velocity decreased to a constant value with relative humidity. The xerogel saturated in water exhibited the lowest transverse wave velocity of all. The transverse wave velocity of the xerogel, soaked in ethanol, was roughly equal to that of the fresh porous xerogel. The longitudinal wave velocity decreased to a minimum at about 35% RH and then increased with further adsorption of moisture. The xerogel soaked in ethanol exhibited the highest longitudinal wave velocity. Values of wave velocities for the sample equilibrated at 25% RH following 55% RH fall fairly close to the previously established curve.

In Table 2, the elastic constants calculated from the matrix bulk density are listed. Figure 2 illustrates the change in elastic constants as relative humidity was increased to 55% RH. Figure 3 illustrates the change in Poisson's ratio over the same interval. Young's modulus exhibits a minimum at about 35% RH. The shear modulus decreases to a constant value at 35% RH and greater.



The bulk modulus exhibits a minimum between about 15 and 35% RH. Poisson's ratio exhibits a minimum of 0.164 at about 15% RH. Poisson's ratio for fully dense silica is 0.16. Values of elastic constants for the sample cycled to 25% RH following 55% RH are slightly above the indicated curve.

In Table 3 the elastic constants calculated from values of total bulk density are listed. The Young's modulus and shear modulus exhibit minima between about 15% and 35% RH. The bulk modulus exhibits a minimum at about 15% RH. Values of Poisson's ratio are identical to those of Table 2 because calculations of this quantity are unaffected by choice of bulk density.

### Discussion

The values of weight gain observed here are roughly three times greater than those reported in a previous study in which elastic properties were measured as a function of relative humidity (3). In this study, xerogels were outgassed at 250°C, a temperature near the optimum for achieving high surface area (16), while in the previous study drying was accomplished at ambient temperature with dry air. It is likely that the difference in weight gain is due to the difference in drying techniques. The xerogels in this study were substantially drier prior to exposure to atmospheric moisture, while those of the previous study contained a large amount of adsorbed water or solvents remaining from synthesis.

When water is adsorbed on silica as H<sub>2</sub>O molecules or as hydroxyl groups, it can attack siloxane bonds and convert them into silanols (16). The concentration of hydroxyls on silica surfaces varies from 4 to 10 hydroxyls per nm<sup>2</sup>. Hydroxyl groups can also be dissolved in the silica network. Hydroxyl groups are not removed with low temperature drying under vacuum or with drying at temperatures as high as 150°C. At temperatures over about 170°C, hydroxyl

groups begin to be removed. At a drying temperature of 300°C, the specific surface area of a microporous silica gel exhibits a maximum (16). With drying at 400°C, the total hydroxyl concentration can be halved. Upon rehydration, siloxanes that were produced by dehydration at temperatures below about 400°C can readily be converted back into silanol groups. In fact, siloxanes that were produced by dehydration at a temperature of 300°C are mostly rehydrated at a relative humidity of only 20%. Above 400-450°C enough hydroxyl groups are removed to leave large siloxane areas that are less easily rehydrated (17). Complete rehydration of silica dehydrated at high temperature may require immersion in boiling water for a few days (16).

What this means in terms of the silica xerogels prepared here is that the outgassing treatment removed some but not all hydroxyls. Because the gels were heated barely to a temperature where dehydration could have converted silanol groups into siloxane bonds, the hydroxylation was largely a surface phenomenon and was reversible. The effect of relative humidity can be treated as an adsorption isotherm where 35% RH corresponds to complete surface coverage and higher levels of relative humidity contribute to pore filling (16).

Accordingly, an interesting trend is observed in the transverse wave velocity. The outgassing temperature of 250°C was sufficient to produce some siloxane bonds. Linear contraction occurred during outgassing at 250°C as a result. When exposed to atmospheric humidity, it is found for xerogels that the transverse wave velocity decreases due to the conversion of some siloxane bonds to silanols. Therefore, as observed, the transverse wave velocity is expected to decrease most rapidly with initial water adsorption until a monolayer hydroxyl coverage is achieved. In contrast, the sample soaked in ethanol shows no change in transverse wave velocity from that of the freshly outgassed gel. Ethanol like other alcohols may be unable to convert siloxane bonds into silanols (18).

The longitudinal wave exhibits a minimum at about 35% RH. This trend may be attributed to the competing effects of stress corrosion and pore filling. Following the same reasoning as above, the decrease in velocity with moisture adsorption is expected to be most rapid initially. The increase in longitudinal wave velocity but not transverse wave velocity upon further addition of moisture may be due to pore filling. Filling of pores with liquid increases longitudinal wave velocity by preventing longitudinal compression of the silica skeleton. Previously, it was observed that longitudinal wave velocity increased with relative humidity and this result was attributed to pore filling (3). The xerogel contains pores mostly of size between about 0.8 and 1.6 nm. Such pores can contain at most a few monolayers of adsorbed moisture. At about 35% RH, the weight gain is one half of the total, and pore filling begins with the smallest pores. The sample soaked in ethanol would be expected to have the highest longitudinal velocity of all, as observed, because of complete pore filling without prior stress corrosion.

The values of elastic constants as calculated from the matrix bulk density (Table 2) are more simply explained than those calculated from total bulk density (Table 3). The shear modulus calculated from the matrix bulk density decreases with increasing relative humidity because the transverse wave velocity decreases with increasing adsorption of hydroxyls. When pore filling begins, the transverse wave velocity is unaffected because a liquid will not support shearing. The shear modulus should parallel the transverse wave velocity. The shear modulus calculated from total bulk density does not.

Calculations based on total bulk density which includes weight gain are more common than calculations based on the matrix bulk density. Calculations of elastic constants are conventionally made with total bulk density with the necessary assumption that the adsorbed species vibrate along with the matrix and

therefore contribute to the vibrating mass. The mega hertz driving frequency used here is much lower than the natural frequency of the adsorbed molecules and therefore these molecules would be expected to vibrate with an amplitude equal to that of the matrix. Nevertheless, calculations of the shear modulus according to total bulk density leads to a minimum in shear modulus at 35% RH where the shear modulus should decrease to a constant value for 35% RH and greater. Therefore, the calculations according to matrix bulk density show the correct trend.

The linear contraction of xerogels as they age is at least partly irreversible. The values of elastic constants calculated at 25% RH following exposure to 55% RH are slightly above the trend established on adsorption. This means that densification due to aging is a relatively minor effect.

### Conclusions

The difference between the results of this study and those of the previous study (3) can be attributed to the difference in the drying techniques. The dehydration treatment described here produced siloxanes which converted to silanols upon exposure to atmospheric moisture. The decrease in transverse wave velocity as well as longitudinal wave velocity was attributed to this weakening of the silica network. Once the silica surface achieved a monolayer coverage, further adsorption led to pore filling. Beyond 35% RH, the longitudinal wave velocity increased while the transverse wave velocity stayed the same.

### Acknowledgement

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Table 1: Wave Velocities

Sample	$v_L$ (km/sec)	$v_T$ (km/sec)
Freshly outgassed	2.25	1.40
15% RH	1.95	1.24
25% RH*	1.91	1.18
35% RH	1.88	1.16
55% RH	2.00	1.12
Soaked in water	2.27	1.08
Soaked in ethanol	2.53	1.37

Table 2: Elastic constants calculated from matrix bulk density

Samples	E(GPa)	G(GPa)	K(GPa)	n
Freshly outgassed	4.91	2.07	2.59	0.184
15% RH	3.77	1.62	1.87	0.164
25% RH*	3.79	1.60	2.02	0.187
35% RH	3.42	1.43	1.87	0.194
55% RH	3.60	1.42	2.63	0.272
Soaked in water	3.20	1.18	3.66	0.354
Soaked in ethanol	5.03	1.94	4.08	0.295

Table 3: Elastic constants calculated from total bulk density

Samples	E(GPa)	G(GPa)	K(GPa)	n
Freshly soaked	4.91	2.07	2.59	0.184
15% RH	4.23	1.81	2.10	0.164
25% RH*	4.39	1.85	2.34	0.187
35% RH	4.27	1.79	2.33	0.194
55% RH	4.86	1.91	3.54	0.272
Soaked in water	4.84	1.79	5.53	0.354
Soaked in ethanol	7.01	2.71	5.69	0.295

\*Sample returned to 25% RH from 55% RH

### List of Figures

- Figure 1. Wave velocities vs relative humidity.
- Figure 2. Elastic constants vs relative humidity.
- Figure 3. Poisson's ratio vs relative humidity.

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